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The Effect of Solvent Type on the Infrared Spectrum of
Carbon Monoxide Adsorbed
Species Selective Gas Chromatographic Detectors

by

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The Effect of Solvent Type On the Infrared
Spectrum of Carbon Monoxide Adsorbed at
Platinum Electrodes

Mark R. Anderson, Daniel Blackwood, and B. Stanley Pons

Abstract

* *

The infrared spectrum of CO adsorbed on a platinum electrode from several solvents was investigated. In N-methylformamide, acetonitrile, and 1,2-dichloroethane, the infrared band attributed to linear bonded CO had experimental Stark tuning rates of $20\ cm^{-1}/V$, $22\ cm^{-1}/V$, and $19\ cm^{-1}/V$, respectively. For each of these solvents, the potential dependence of the band position was found to be linear for the entire potential range investigated. When methanol was the solvent, the plot of the band position versus potential had three distinctly linear portions, each with a different value for the slope. The behavior is explained in terms of the ability of the solvent molecules to closely approach the electrode surface, the polarity of the solvent, and the orientation of solvent molecules with respect to the polarization of the electrode.

The Effect of Solvent Type On the Infrared
Spectrum of Carbon Monoxide Adsorbed at
Platinum Electrodes

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INTRODUCTION

The infrared spectrum of carbon monoxide adsorbed on a platinum electrode from aqueous solutions has been extensively studied (1-8). A strong band is observed at about 2070 cm^{-1}, and has been assigned to the CO stretch vibration of a molecule which is linearly bound in an on-top site. The frequency of this band is observed to shift with applied potential at a rate of 30 cm^{-1}/V (3,4). The shift has been explained in terms of (a) a molecular orbital model where changes in the carbon-oxygen bond strength occur as the degree of back-bonding from the 5d electrons of the metal to the $2\pi^*$ antibonding orbitals is changed with electrode potential (the "chemical" effect) (3,9), and (b) by the effect of the electromagnetic field near the electrode on the bond order (the electrochemical "Stark" effect) (10-14).

Recently the potential dependent frequency shift has been observed to be significantly smaller in organic solvents (approximately 20 cm^{-1}/V) than when the solvent is water (15). The purpose of this paper is to explore the cause of the solvent effect on the potential dependent frequency shift.

EXPERIMENTAL

Tetraethylammonium vanadiumhexacarbonyl was prepared and purified by standard procedures. The resulting yellow powder was found to be stable for days at room temperature and in the presence of atmospheric oxygen. Acetonitrile (Aldrich Gold Label), 1,2-dichloroethane (EM Scientific), methanol (J. T. Baker Chemical Co.), and N-methylformamide (Fluka) were used as supplied. All glassware was cleaned in a 50:50 (V:V) mixture of HNO$_3$ and H$_2$SO$_4$, rinsed with triply distilled water, steamed (triply distilled water) for half an hour, rinsed with acetone, and dried in an oven at 35°C.

For the infrared experiments, a thin layer cell of the type previously described was used (16). The technique used to acquire all the data shown in the paper was Subtractively Normalized

Interfacial Fourier Transform Infrared Spectroscopy (SNIFTIRS). The FTIR spectrometer used was a vacuum bench Bruker/IBM IR/98.

The surface of the platinum electrode was prepared by polishing with successively finer grades of alumina, down to 0.05 micron, to obtain a mirror finish. The electrode was then placed into the electrolyte, and the solution was deoxygenated for 20 minutes. After deoxygenation, the electrode was cycled between -0.80 V and 1.00 V vs. SCE at 10 mV/s in the positive direction and 3 V/s in the negative scan direction for five minutes. The electrode was then pushed against the infrared transparent CaF_2 window to form a thin layer cell.

The supporting electrolyte was 0.10 mol dm^{-3} $LiClO_4$ in all solvents except in solutions of 1,2-dichloroethane, where the supporting electrolyte used was 0.10 mol dm^{-3} tetrabutylammonium tetrafluoroborate. The change was necessary because of the solubility of the metal perchlorate in this solvent.

Carbon monoxide was adsorbed on the platinum surface via the oxidation and subsequent decomposition of $V(CO)_6^-$ as previously explained (14).

RESULTS AND DISCUSSION

The intent of the investigation was to study the potential dependent frequency shift of linearly bonded carbon monoxide on a platinum surface as a function of bulk dielectric constant of the solvent (Table 1). Figure 1 is an example of a SNIFTIRS spectrum obtained during the investigations. In aqueous electrolyte, a significantly larger frequency shift was observed than in any of the organic solvents (Table 1), including N-methylformamide which has a much larger *bulk* dielectric constant than water (182 vs. 78). This observation was somewhat surprising because, as Lambert has theoretically shown, the Stark tuning rate is dependent upon the solvent dielectric constant (11):

$$d\nu/dV = d\nu/dE \times C/\epsilon \qquad\qquad [1]$$

where $d\nu/dV$ is the frequency shift with change in electrode potential, $d\nu/dE$ is the frequency shift with change in the electric field strength (for platinum electrodes Lambert calculates a value of the tuning rate of 1.1×10^{-6} $cm^{-1}/(V/cm)$), C is the double layer capacitance, and ϵ is the solvent permittivity. The value of the dielectric constant in Lambert's derivation, however, is that of the solvent in the double layer. In the double layer region, the dielectric constant of the solvent is different from the bulk value due to electrostriction of the solvent in the presence of relatively large electric field strengths. The high electric field strength reduces the random orientation of dipolar solvent molecules causing the dipoles to line up in the direction of the field lines. This loss of the random solvent structure results in a decrease in the solvent permittivity. Electrostriction has been demonstrated for water (17,18) as well as for other solvents (19). Apparently, solvent properties in addition to the dielectric constant contribute to the Stark tuning rate.

In order for a Stark tuning mechanism to cause a shift in the frequency of a vibrational mode in an adsorbed species, it has been calculated that fields on the order of 3×10^{7} V/cm and greater would be required (10,11,19). Generally, such large fields are likely to occur only within approximately 0.3 nm of the electrode surface. The extent to which the solvent molecules can influence the Stark tuning rate, therefore, depends upon the ability of the solvent to approach the electrode surface close to this distance as well as the magnitude of the solvent dielectric constant and the polarizibility of the solvent. As most solvent molecules have characteristic sizes larger than 0.3 nm, it is likely that the internal polarity of the molecule near the electrode surface will exert more of an influence on the magnitude of the Stark tuning rate than the bulk dielectric constant

In the case of adsorbed carbon monoxide, the sum of the Pt-C and C=O bond lengths will be about 0.3 nm; most of the adsorbed system is under the full influence of the field drop at the interface. For high surface coverages of CO, the region close to the electrode surface will be blocked for approach of the larger solvent molecules; therefore, solvent molecules will be unable

to locate close to the strong potential gradient. Adsorbed CO is well known to poison platinum electrode surfaces to electrochemical reactions by blocking access to the electrode of the electroactive species (21,22). This effect is dramatically demonstrated when observing the voltammetry for the hydrogen evolution reaction in methanol solvent at a platinum electrode in the presence and absence of adsorbed CO (Figure 2). The reaction is effectively suppressed when the electrode is highly covered with CO. In terms of the proposed model, it is likely that only water, which has small molecular dimensions and is highly polar, is capable of approaching close enough to the platinum electrode to make a significant difference to the system permittivity in the region very close to the electrode and thus affect the Stark tuning rate.

The frequency shifts for all the organic solvents, with the exception of methanol at potentials below 0.20 V vs. SCE, gave rise to the same approximate value for the Stark tuning rate (all were within 3 cm^{-1}/V of 20 cm^{-1}/V, which is only a little larger than the experimental error), despite very large differences in the dielectric constants. It is proposed that a value of about 20 cm^{-1}/V is the natural tuning rate (the situation where solvent is excluded from the electrode surface) for the CO stretch of linearly adsorbed carbon monoxide at a platinum electrode. The nature of the solvent determines whether or not the experimentally measured Stark tuning rate differs from 20 cm^{-1}/V. The large organic solvents are unable to approach to within 0.3 nm of the electrode; consequently, they have no effect upon the Stark tuning rate.

When methanol is used as the solvent, the behavior is dramatically different than for the other solvents investigated. Unlike other solvents, the rate of movement of the adsorbed CO band frequency in methanol is not linear with potential over the entire region investigated. Rather, three distinct regions are found (Figure 3). For potentials negative of 0.20 V vs. SCE, the frequency shift with potential is approximately linear and has a slope of 25 cm^{-1}/V. This slope was the largest found for any of the organic solvents investigated. Between 0.20 V and 0.40 V vs. SCE, the CO frequency becomes virtually independent of potential. Finally, for electrode potentials more positive

than 0.40 V v̲s̲. SCE, the linear potential dependence resumes and has a slope of about 20 cm^{-1}/V. Throughout the entire potential region, the peak intensity of the CO bands remains constant. This observation indicates that no change in the CO surface coverage is occurring during the measurements. The behavior of the CO spectrum in the presence of methanol may be explained in terms of a reorientation of the methanol molecules with respect to the electrode surface.

At potentials negative of the point of zero charge, it is likely that the OH group of the methanol will be oriented towards the electrode. The OH group is both the most polar and the least hindered part of the molecule, thus allowing the methanol molecule to approach within the critical 0.3 nm region from the electrode surface. Such a close approach alters the Stark tuning rate to 25 cm^{-1}/V. When the platinum surface is positive with respect to the point of zero charge, however, the hydrogen on the OH group will be repelled from the surface causing the nonpolar and relatively large methyl group to face the electrode surface. Under these conditions the system behavior is like the other organic solvents, and a shift of 20 cm^{-1}/V is experimentally observed. From this data, the potential of zero charge is estimated to be approximately 0.3 V v̲s̲. SCE. Unfortunately, attempts to independently measure the point of zero charge by capacitance techniques proved unsuccessful as no obvious capacitance maximum was observed. The electrical structure of the double layer is pictured as being dominated by the CO dipole interaction with the surface, while the methanol reorientation is a second order weak electrostatic interaction. We also point out that the autoprotolysis of methanol

$$2MeOH \rightleftharpoons MeO^- + MeOH_2^+$$

like that of water, is significant and may influence the permittivity of the 0.3nm region. This point is the subject of further study.

A consequence of the proposed mechanism is that nonlinearities in the frequency shift would be expected in other solvents if the potential region investigated included the potential of zero charge and if solvent molecules contained small regions of high polarity that were not sterically hindered from approaching the close regions of the metal surface. None of the other solvents investigated in this study met these conditions. In addition, specific adsorption of small cations or anions may also have an effect upon the Stark tuning rate due to their ability to penetrate the critical region close to the electrode surface. Some investigations have reported electrolyte effects upon the experimental Stark tuning rate for adsorbed CO (3,22). Other studies, however, have found no effect due to the electrolyte identity upon the Stark tuning rate (5). This topic is the subject of continued study. In our studies large electrolyte ions (or highly solvated lithium ion) which do not specifically adsorb were used and the nature of the supporting electrolyte had no effect upon the spectrum (14).

The effect of a mixed aqueous/organic solvent on the potential dependent frequency shift was also investigated. Acetonitrile was chosen as the organic solvent for this investigation since it is miscible with water in all proportions and exhibits the expected 22 cm^{-1}/V shift typical of organic solvents over the whole potential range examined. Figure 4 shows a plot of the measured frequency shift versus percentage of water, by volume, in the electrolyte. It can be seen that a transition occurs from the behavior expected from a pure organic solvent to that expected for a pure aqueous solution at approximately 23% water and that the transition occurs rapidly over only a 3% change in the water concentration. This result suggests that in the double layer region, or at least the inner Helmholtz plane, the water and acetonitrile molecules are essentially separated. Only at relatively high concentrations is the water able to displace the acetonitrile and approach the electrode surface This result was unexpected as the miscibility of acetonitrile and water would suggest a homogeneous solution.

CONCLUSIONS

A Stark tuning rate for CO adsorbed on platinum without the influence of solvent or electrolyte in the inner Helmholtz layer has been measured to be approximately 20 cm^{-1}/V. Solvent molecules can only alter the magnitude of the Stark tuning rate of linearly bonded CO molecules if they are able to approach within 0.3 nm of the electrode surface. In the current research only water and methanol solvents were found to significantly alter the value of the Stark tuning rate from this base value. The effect is believed to increase with increasing polarity of the portion of the solvent molecule which is within this critical region. Large organic solvent molecules are hindered from approaching to within the critical distance of the electrode surface by the adsorbed layer of CO. As a result, a potential dependent frequency shift of only 20 cm^{-1}/V is obtained in the presence of organic solvents irrespective of the value of the bulk dielectric constant.

ACKNOWLEDGEMENT

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Table 1. Experimental Stark Tuning Rate for the Solvents Investigated.

Solvent	Bulk Dielectric Constant	Stark Tuning Rate
1,2-Dichloroethane	10.9	19 cm^{-1}/V
Methanol (E > 0.4V)	32	20
Methanol (E < 0.2V)	32	25
Acetonitrile	36	22
Water	78	30
N-methylformamide	182	22

FIGURE CAPTIONS

Figure 1.   SNIFTIRS spectra of linear bonded CO in the presence of 0.10 $\underline{M}$ LiClO$_4$/Acetonitrile.

Figure 2.   Cyclic voltammogram showing the hydrogen evolution reaction for methanol solvent with 0.10 $\underline{M}$ LiClO$_4$ (a) in the presence of adsorbed CO and (b) in the absence of adsorbed CO.

Figure 3.   A plot of the peak position as a function of electrode potential for linear bonded CO in the presence of 0.10 $\underline{M}$ LiClO$_4$/methanol.

Figure 4.   A plot of the experimental Stark tuning rate as a function of percentage of water present in a 0.10 $\underline{M}$ LiClO$_4$/ acetonitrile solution.
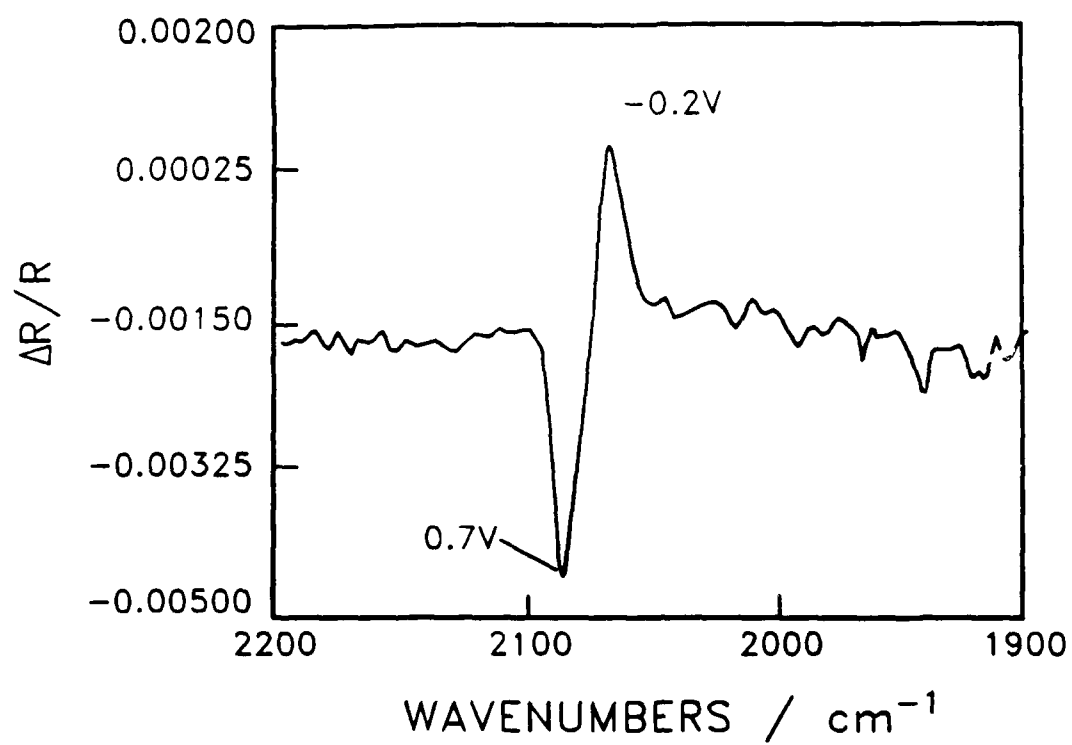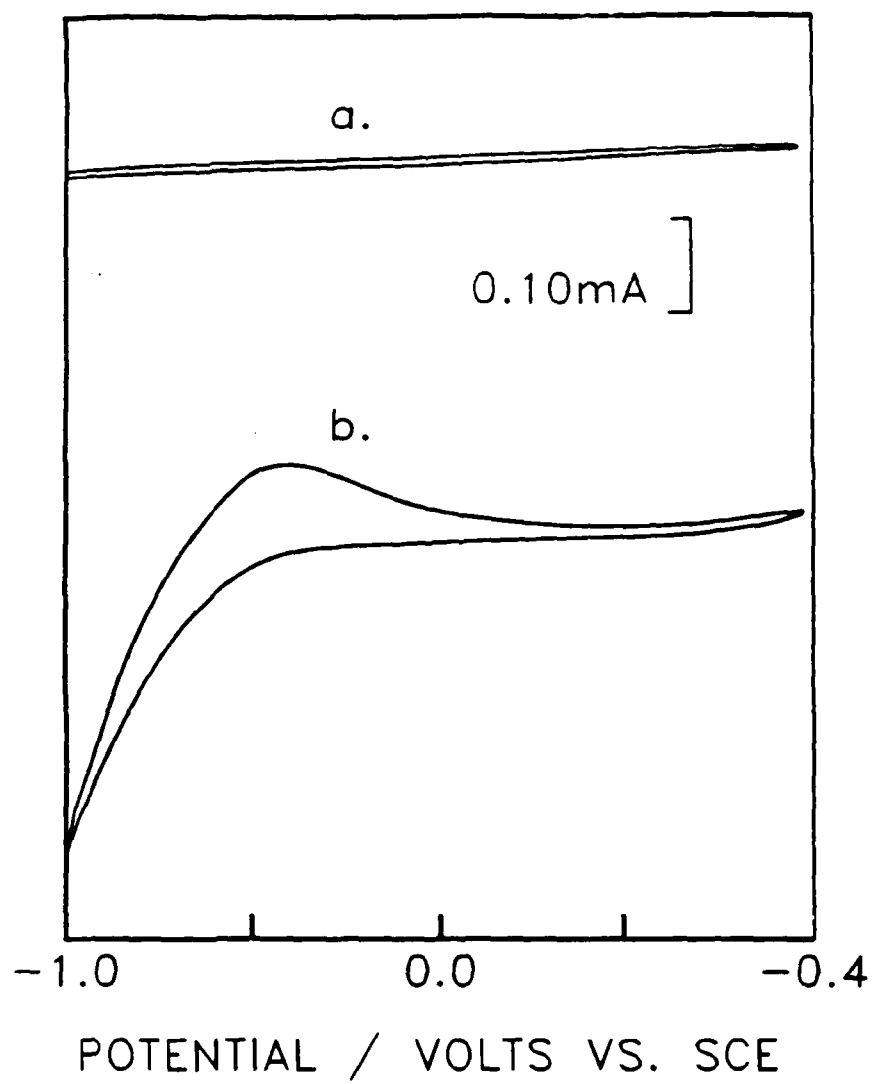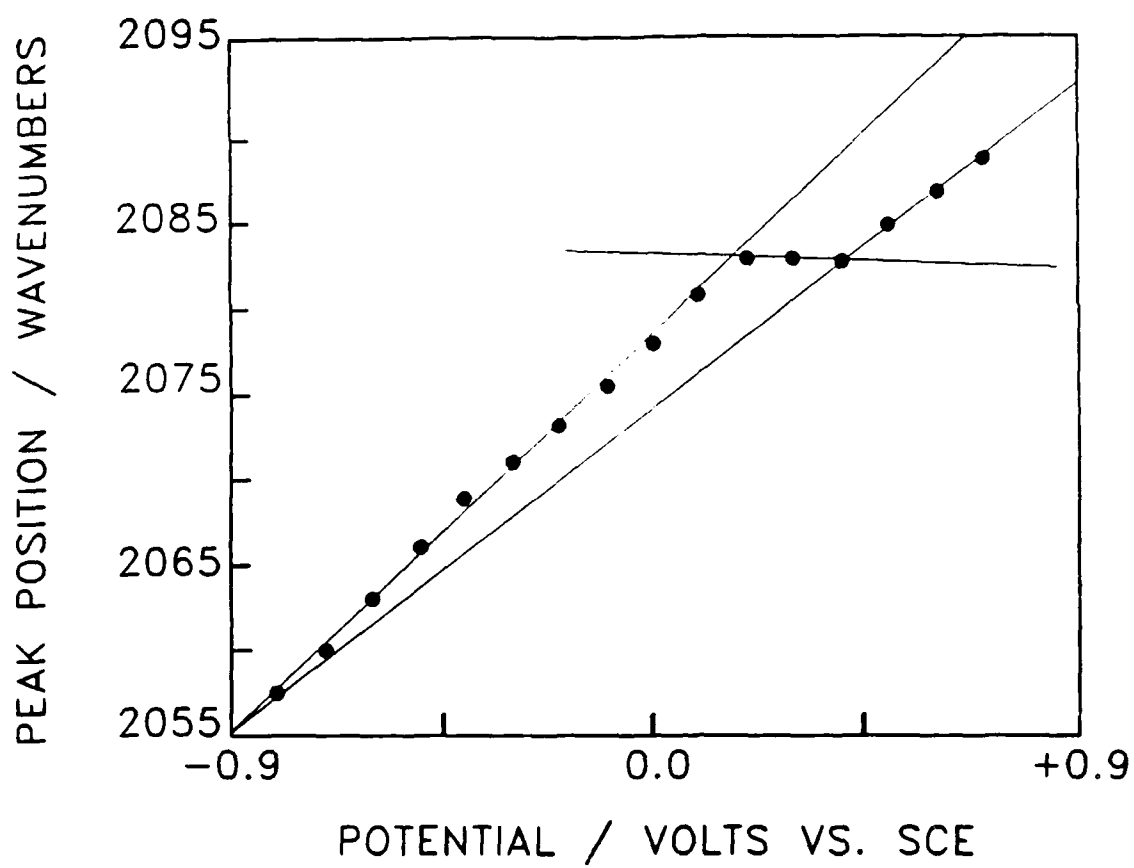
Fig 1

a.

0.10mA]

b.

-1.0   0.0   -0.4

POTENTIAL / VOLTS VS. SCE

FIG

Fig
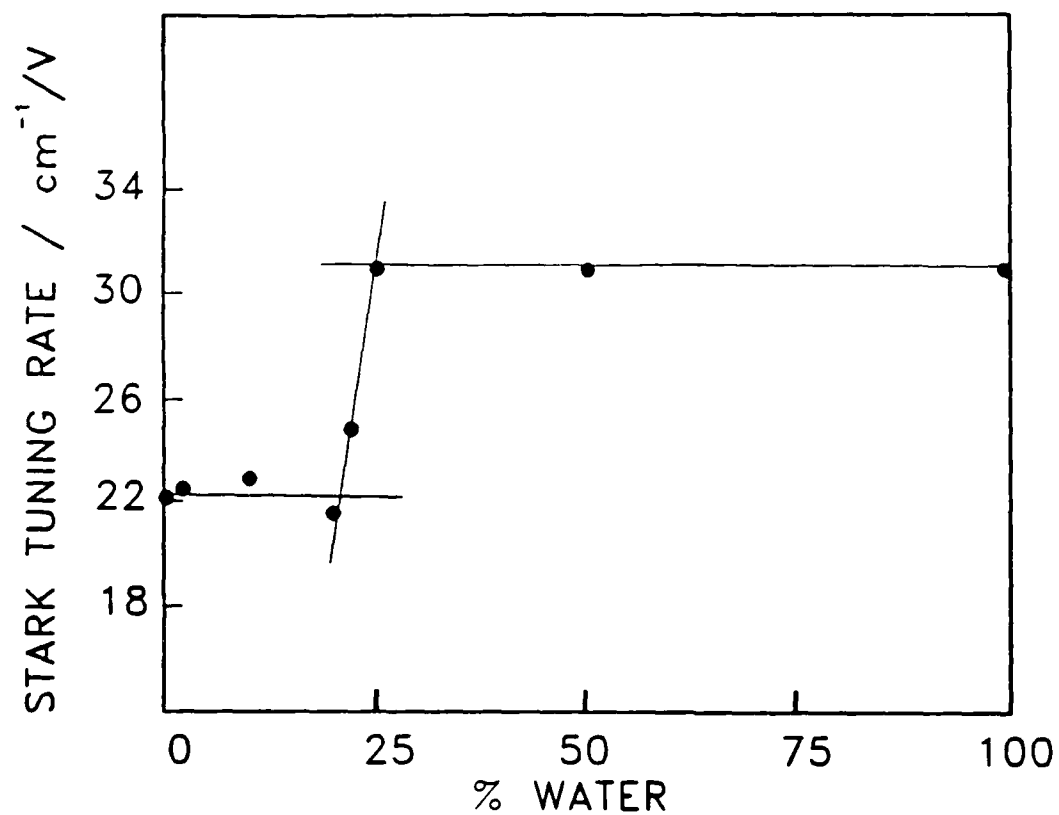
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